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Preparation of Urethane Oils from Microwave-Assisted Glycolyzed Products of Waste PET Bottles

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Abstract

Post-consumer PET bottles were depolymerized with propylene glycol at a weight ratio between PET and glycol of 37.5 : 62.5 under microwave energy at irradiation power of 600 watt, using zinc acetate as a catalyst. The glycolyzed product, consisting of oligomeric diols with a hydroxyl value of 253 mg KOH/g, was obtained. Analysis of the glycolyzed product by GPC indicated that it consists of compounds with a number-average molecular weight of 2265. The glycolyzed product was further reacted with linseed oil and toluene diisocyanate to obtain urethane oil at hydroxyl to isocyanate ratio of 1 : 0.8 with methanol acting as a blocking agent. It was found that the obtained urethane oil was a transparent yellowish liquid with low viscosity. The prepared urethane oil was characterized for molecular weight and its properties were determined and compared with those of the conventional and commercial urethane oils. Results showed that the properties of waste PET bottles-based urethane oil were comparable to those of the commercial urethane oil.

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Keywords: Recycling; Waste PET bottles; Microwave-assisted glycolysis; Oligomeric diols; Urethane oil

1. Introduction

Poly(ethylene terephthalate) or PET is one of the versatile engineering plastics and shows excellent thermal and mechanical properties. It is a semi-crystalline, thermo-plastic polyester with high strength and transparency. These unique properties make PET extensive use in plastic packaging application,

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especially disposable soft-drink bottles. With the widespread use and increase in consumption, the amount of waste PET is growing rapidly. This has caused serious environmental problems since PET bottles do not readily decompose in nature.

Chemical PET recycling through decomposition and conversion into value added reusable chemical products is one of the important recycling techniques. The chemical recycling of waste PET can be carried out in many processes such as glycolysis, methanolysis, hydrolysis and aminolysis. The two processes that have reached commercial maturity are glycolysis and aminolysis [1]. However, these conventional processes required high temperature and long reaction time. In the last decade, the use of microwave irradiation as an energy source in chemical reactions has been developed. Microwave provides a number of advantages over the conventional heating such as noncontact, instantaneous and rapid heating rate that results in reduced reaction time [2]. Li, K et al. [3] used microwave irradiation for hydrolytic depolymerization of PET in the presence of different catalysts. Among of the catalysts used in the reaction, zinc acetate was demonstrated as the most effective catalyst and the depolymerization rate nearly reached to 100% with high yields of bis(hydroxylethyl)terephthalate (BHET) and glycols. Pingale and Shukla's studies on glycolysis of PET bottle waste using microwave irradiation in the presence of several catalysts showed that the reaction time reduced to 35 min compared to 8 h under conventional heating system [4].

PET glycolysis carried out using different glycols in the presence of a catalyst results in oligomeric diols which can be used as reactants for preparation of other polymers such as unsaturated polyester resin, polyurethane, polymer concrete and urethane oil. Urethane oil or urethane alkyd is generally prepared from the reaction between diisocyanate and a mixture of mono- and di-glycerides resulting from alcoholysis between oils and glycerol. By substituting glycerol in the reaction with these glycolyzed products, urethane oils are obtained. From previous works [5], [6], waste PET bottles were depolymerized by glycolysis in excess propylene glycol and the resulting glycolyzed products were then reacted with soybean oil or palm oil and toluene diisocyanate to obtain urethane oils. The properties of the synthesized urethane oils were comparable to those of the commercial urethane oil.

In the present work, the glycolysis of waste PET bottles with propylene glycol under microwave irradiation was employed. The obtained glycolyzed products were used for preparation of urethane oil. The properties of the prepared urethane oil were investigated and compared with those of the glycerol based conventional and commercial urethane oils.

2. Experimental Procedure

2.1 Materials

Waste PET flakes were obtained by grinding post-consumer bottles. Laboratory-grade propylene glycol (PG, 1,2-propane diol) was purchased from Ajax Chemical (Auburn, NSW, Australia). Glycerol, zinc acetate, calcium oxide (CaO), and methanol were purchased from Fluka (Buchs, Switzerland). Linseed oil, drier, toluene diisocyanate (TDI 80/20; consisting of 80% 2,4- and 20% 2,6-isomers) and commercial urethane oil were supplied by Siam Chemical Industries Co., Ltd. (Samutprakarn, Thailand). Xylene was purchased from Labscan Asia (Bangkok, Thailand). All other materials were used as received without further purification.

2.2 Glycolysis of wasted PET bottles

Waste PET flakes, PG (ratio of PET : PG = 37.5 : 62.5 w/w), and zinc acetate (0.5% w/w of PET) were mixed in a 500-mL one-neck round-bottom flask. The mixture was heated under reflux in a domestic

oven at irradiation power of 600 watts for 35 min. After that, the mixture was allowed to cool to room temperature and the glycolyzed product (GP) was obtained.

2.3 Synthesis of urethane oils

The amounts of all materials used in this step are given in Table 1. The glycolyzed product and linseed oil were mixed in a 500-mL four-neck round-bottom flask equipped with a stirrer, a thermometer and a reflux condenser. The mixture was stirred and heated to 200°C under nitrogen atmosphere followed by the addition of CaO (0.1% w/w of polyol). The temperature was then raised to 245°C and the mixture was maintained at this temperature until a sample (1 part) was soluble in ethanol (2 parts). The mixture was cooled to 50°C, after which xylene at half of the amount in Table 1 was added. A solution of TDI and drier in another half amount of xylene was then slowly added. The mixture was heated at 75 to 80°C for 2 h. Methanol was finally added and the urethane oil was obtained. In order to investigate the effect of polyols on the properties of urethane oil, conventional glycerol-based urethane oil was also prepared.

Table 1. Formulas for synthesizing urethane oils.

Formulas	GP *(g)*	Glycerol *(g)*	Linseed oil *(g)*	TDI *(g)*	Xylene *(g)*	Drier *(g)*	Methanol *(g)*
GP-based urethane oil	100	-	100.98	39.46	103.04	0.1	1
Conventional urethane oil	-	100	236	226	240.8	0.1	1

2.4 Characterization

The hydroxyl value of the glycolyzed product was determined based on ASTM D 2849 (Method C). The chemical structures of the glycolyzed product and urethane oils were analyzed using a Nicolet FTIR spectrophotometer (Model Thermo Nicolet NEXUS 670; Nicolet Instrument. Inc., Madison, WI, USA). Their molecular weights and molecular weight distributions were also characterized by a GPC system (Shimadzu class-VP, Shimadzu Scientific Instruments, Columbia, MD, USA) using THF as solvent with an injection rate of 1 mL/min at 30°C. The viscosities were determined using a Brookfield DV-III programmable viscometer (Brookfield Engineering Labs, Stoughton, MA USA). Acid values were calculated based on ASTM D1639. The colors of the obtained urethane oils were determined by comparison with the colors of standard Gardner solutions. Their solubility in several solvents was also tested.

2.5 Determination of film properties

Urethane oil films were formed by applying the oils onto tin plate or glass panels, depending on each standard test method, using a film applicator. The samples were then subjected to the following tests, including hardness (using a mechanical scratch test apparatus; Sheen Instruments Ltd., Surrey, UK), flexibility (using a conical mandrel test apparatus; Sheen Instruments Ltd.), and adhesion (using a crosscut tape method based on ASTM D3359 Method B). Furthermore, water and alkali resistances were also determined by immersing the coated panels in water and 5%NaOH for 24 h and the samples were

examined every 30 min for film blistering. Their properties were then compared with those of the prepared conventional and commercial urethane oil supplied by Siam Chemical Industries Co., Ltd.

3. Results and discussion

Glycolyzed product obtained from glycolysis of waste PET bottles in excess PG under microwave irradiation was a blue-green transparent viscous liquid. Its FT-IR spectrum shown in Figure 1(a) exhibits peaks corresponding to O-H stretching, C-H stretching, C=O stretching, C-O-C stretching and C-OH stretching at wavenumbers of 3450, 2980, 1720, 1275, and 1046 cm^{-1}, respectively. This indicates the presence of compound and/or compounds having hydroxyl and ester groups. GPC analysis indicated that the number-average molecular weight of this glycolyzed product was 2265. This result differs from that obtained by conventional heating glycolysis [5], [6], giving higher molecular weight product (2,265 versus 240-1107). It was previously reported that glycolyzed products of PET and PG usually composed of BHET, BHPT, α-(2-hydroxyethyl)-α'-(2-hydroxypropyl) terephthalate, and their dimers, trimers, and oligomers [5]-[7]. Therefore, this obtained glycolyzed product possibly consists of oligomers of these products. The glycolyzed product had a hydroxyl value of 253 mg KOH/g, hence, there is unreacted PG in the product.

The mixture of mono- and di-glycerides obtained from alcoholysis of linseed oil with the glycolyzed product exhibits FT-IR spectrum having peaks corresponding to those observed in FT-IR spectra of the glycolyzed product and linseed oil as shown in Figure 1. The existence of mono- and diglycerides was confirmed by their complete solubility in ethanol.

As illustrated in Figure 2, the glycolyzed product-based and conventional urethane oils exhibit the similar spectra to that of the commercial urethane oil. The characteristic peaks of urethane bonds appear at wavenumbers of 3341, 1732, and 1538 cm^{-1}. However, the FT-IR spectra of the synthesized urethane oils show the characteristic peak of unreacted NCO groups at 2273 cm^{-1}, which is not observed in the FT-IR spectrum of the commercial urethane oil.

The molecular weights and molecular weight distributions of these urethane oils are given in Table 2. It was found that the conventional glycerol-based urethane oil has higher molecular weight than the glycolyzed product-based urethane oil. This may be due to the presence of higher amounts of reactive

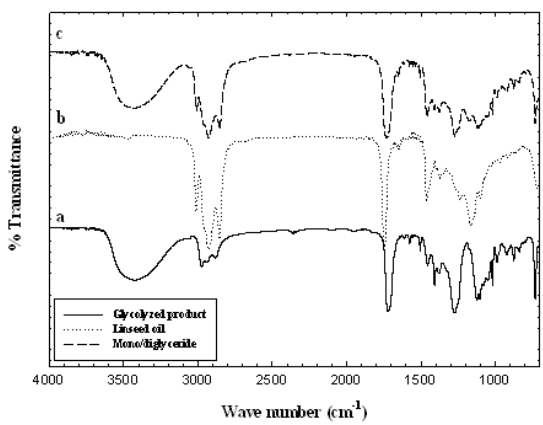

Fig. 1. FT-IR spectra of (a) glycolyzed product, (b) linseed oil, and (c) mono/diglycerides.

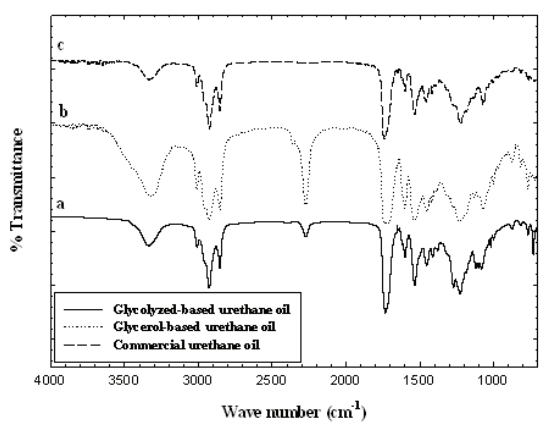

Fig. 2. FT-IR spectra of (a) GP-based urethane oil, (b) conventional, and (c) commercial urethane oil.

Table 2. Molecular weights and molecular weight distributions of synthesized and commercial urethane oils.

Formula	M_n	M_w	MWD
GP-based urethane oil	3,089	3,556	1.15
Conventional urethane oil	3,120	5,116	1.64
Commercial urethane oil	7,029	41,178	5.86

functional groups in the prepared conventional urethane oil as shown in Table 1. Moreover, it can be seen that the molecular weights of both the synthesized urethane oils are lower than that of the commercial one. This may be caused by the differences in the types of reactants and the reaction conditions used in urethane oil synthesis.

Both synthesized urethane oils were transparent yellowish liquids with different viscosities varying with their molecular weights as indicated in Table 3. Their acid values are in the range of 0.2-0.6. Table 3 also shows that both the synthesized urethane oils are darker than that of the commercial one. The glycolyzed product-based urethane oil is soluble in aromatic nonpolar solvent such as xylene but not in aliphatic nonpolar solvent such as white spirit and high polar solvent such as n-butanol. This solubility property is slightly different from that of the conventional and commercial urethane oils which are soluble in both aliphatic and aromatic nonpolar solvent. This might be due to the differences in the compositions and the types of reactants used in urethane oil synthesis. The chemical structures of the glycolyzed product-based urethane oil consists mainly of aromatic constituents (from glycolyzed product and TDI); thus, it is soluble only in aromatic nonpolar solvent. On the other hand, the chemical structure of the conventional and commercial urethane oils consist of both aliphatic and aromatic constituents; as a result, they are soluble in both aliphatic and aromatic nonpolar solvents.

Table 3. Characteristics of synthesized and commercial urethane oils.

Formula	Color (Gardner)	Viscosity (cP)	Acid value (mg KOH/g)	Solubility[a]		
				White spirit	Xylene	n-Butanol
GP-based urethane oil	8+	1,485	0.3	X	√	X
Conventional urethane oil	8+	1,590	0.6	√	√	X
Commercial urethane oil	6	1,810	0.5	√	√	X

[a] √, soluble; X, insoluble

The mechanical properties of urethane oil films were determined and summarized in Table 4. Results show that the film derived from glycolyzed product-based urethane oil has good hardness, excellent flexibility and adhesion, and high impact resistance. It also has excellent water resistance but only fair alkali resistance as can be seen in Table 5. These properties are comparable to those of the films prepared from conventional and commercial urethane oils. All of these results suggest that it is possible to use microwave-assisted glycolyzed product of waste PET bottles to synthesize urethane oil that has the properties comparable to the commercial urethane oil which is currently used.

Table 4. Mechanical properties of urethane oil films.

Property	Formula		
	GP-based urethane oil	Conventional urethane oil	Commercial urethane oil
Hardness (g)	600	700	700
Flexibility (ϕ, mm)	3	3	3
Adhesion	5B	5B	5B
Impact resistance (inch-pound)	160	160	160

Table 5. Water and alkali resistances of urethane oil films.

Substance	Formula		
	GP-based urethane oil	Conventional urethane oil	Commercial urethane oil
Water	Excellent[a]	Excellent[a]	Excellent[a]
Alkali[b]	3:30	3:15	3:00

[a] Films do not change after immersing in distilled water for 24 h at room temperature

[b] Time detected when films exhibited blistering after immersing in 5%NaOH at room temperature.

4. Conclusion

Waste PET bottles were successfully glycolyzed with propylene glycol under microwave irradiation using zinc acetate as a catalyst. The glycolyzed product was then reacted with linseed oil and TDI to obtain urethane oil. An investigation of the properties of glycolyzed product-based urethane oil showed that microwave-assisted glycolyzed product of waste PET bottles could be used as a polyol component in urethane oil preparation.

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